

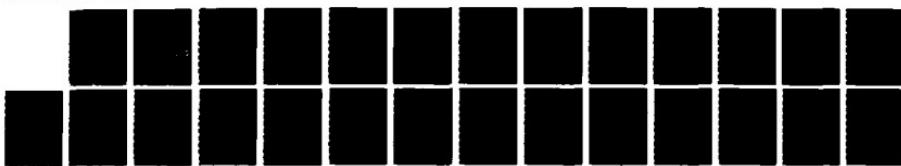
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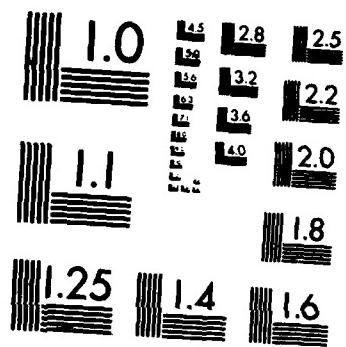
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delocalized bonding with six two-center bonds delocalized in the surface of the octahedron and one six-center core bond as in not only the octahedral boranes, carboranes, and metal carbonyl clusters (e.g.,  $\text{Rh}_6(\text{CO})_{16}$ ) but also the zirconium octahedron clusters with light interstitial atoms such as  $\text{Zr}_6\text{Cl}_{12}\text{Be}$ ,  $\text{Zr}_6\text{Cl}_{13}\text{Be}^-$ ,  $\text{Zr}_6\text{Cl}_{16}\text{Be}^{4-}$ ,  $\text{Zr}_6\text{Cl}_{13}\text{B}$ ,  $\text{Zr}_6\text{Cl}_{14}\text{B}^-$ ,  $\text{Zr}_6\text{Cl}_{15}\text{B}^{2-}$ ,  $\text{Zr}_6\text{Cl}_{14}\text{C}$ , and  $\text{Zr}_6\text{Cl}_{15}\text{N}$  having the general formula  $\text{Zr}_6(\mu_2\text{-Cl})_{12}\text{ECI}_{n-12}^{z+}$  where  $z = 10 - n + pg$  with  $pg$  being the number of valence electrons of the neutral interstitial atom E. The infinite one-dimensional chains of fused octahedra in  $\text{Gd}_2\text{Cl}_3$  as well as the infinite two-dimensional sheets of fused octahedra in the zirconium monohalides have electron and orbital counts corresponding to six-center core bonds in each octahedral cavity and multicenter bonds in the two tetrahedral cavities for each octahedral cavity. A similar bonding model for bulk metals leads to the prediction of maximum heats of atomization for the group 6 metals in accord with experimental observations for the 5d transition series and in only slight disagreement with the experimental maximum heats of atomization of the group 5 metals for the 3d and 4d transition series.

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METAL CLUSTER TOPOLOGY. 5. INFINITE DELOCALIZATION IN ONE AND TWO  
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BUILT FROM FUSED OCTAHEDRA

by

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## Abstract

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This paper shows how graph theory derived models for metal cluster bonding can be extended to infinite one-dimensional chains and infinite two-dimensional sheets of fused metal octahedra using lanthanide and early transition metal halide clusters as examples. Discrete octahedral metal clusters have the following skeletal bonding topologies distinguished by their electron counts: (1) Twelve edge-localized two-center bonds as in the  $\text{Mo}_6(\mu_3\text{-X})_8\text{L}_6^{4+}$  clusters; (2) Eight face-localized three-center bonds as in the  $\text{Nb}_6(\mu_2\text{-X}_{12})\text{L}_6^{2+}$  clusters; (3) Globally delocalized bonding with six two-center bonds delocalized in the surface of the octahedron and one six-center core bond as in ~~not only~~ the octahedral boranes, carboranes, and metal carbonyl clusters (e.g.,  $\text{Rh}_6(\text{CO})_{16}$ ) ~~but also~~ the zirconium octahedron clusters with light interstitial atoms such as  $\text{Zr}_6\text{Cl}_{12}\text{Be}$ ,  $\text{Zr}_6\text{Cl}_{13}\text{Be}^-$ ,  $\text{Zr}_6\text{Cl}_{16}\text{Be}^{4-}$ ,  $\text{Zr}_6\text{Cl}_{13}\text{B}$ ,  $\text{Zr}_6\text{Cl}_{14}\text{B}^-$ ,  $\text{Zr}_6\text{Cl}_{15}\text{B}^{2-}$ ,  $\text{Zr}_6\text{Cl}_{14}\text{C}$ , and  $\text{Zr}_6\text{Cl}_{15}\text{N}$ , having the general formula  $\text{Zr}_6(\mu_2\text{-C})_{12}\text{ECl}_{n-12}^{z+}$  where  $z = 10 - n + \text{PE}$  with PE being the number of valence electrons of the neutral interstitial atom E. The infinite one-dimensional chains of fused octahedra in  $\text{Gd}_2\text{Cl}_3$  as well as the infinite two-dimensional sheets of fused octahedra in the zirconium monohalides have electron and orbital counts corresponding to six-center core bonds in each octahedral cavity and multicenter bonds in the two tetrahedral cavities for each octahedral cavity. A similar bonding model for bulk metals leads to the prediction of maximum heats of atomization for the group 6 metals in accord with experimental observations for the 5d transition series and in only slight disagreement with the experimental maximum heats of atomization of the group 5 metals for the 3d and 4d transition series.

### Introduction

Extensive research during the past 20 years has revealed a rich variety of intriguing metal cluster structures.<sup>2</sup> The diversity of such compounds has inspired numerous efforts to explain their structures and bonding based on approaches such as extended Hückel calculations,<sup>3-5</sup> the skeletal electron pair theory,<sup>6-12</sup> graph-theory derived methods,<sup>1,13-21</sup> the spherical shell theory,<sup>22-24</sup> the topological electron counting method,<sup>25-29</sup> and electron density of states calculations.<sup>30,31</sup> In this connection a question of continuing interest is the relationship between discrete metal clusters and bulk metal structures. This paper shows how the graph-theory derived method for the study of discrete metal cluster bonding topology<sup>13-15</sup> can be extended to one-dimensional and two-dimensional infinite systems and in the ultimate limit of infinite extension in all three dimensions corresponding to bulk metals gives results consistent with experimental information on the heats of atomization of metals.<sup>32</sup>

This paper illustrates these ideas by using early transition metal and lanthanide halides built from fused octahedra having face capping halogen atoms.<sup>33-37</sup> Among such compounds are species consisting of infinite chains of edge-sharing octahedra (e.g.,  $\text{Gd}_2\text{Cl}_3$ )<sup>38</sup> as well as infinite sheets of fused octahedra (e.g., zirconium monohalides)<sup>39</sup> which represent the cubic and hexagonal close packed metal structures extended infinitely in only one and two dimensions, respectively, rather than the full three dimensions. Also the fusion of metal octahedra in such infinite chains and sheets in early transition metal and lanthanide halides involves features different from the fusion of metal octahedra in ruthenium, osmium, and rhodium carbonyls which have been treated by skeletal electron pair<sup>40,41</sup> and topological/graph-theoretical<sup>1,20,42</sup> methods.

### Background

The skeletal bonding topology of a metal cluster consists of a set containing two-electron two-center bonds and/or two-electron multicenter bonds, the latter involving overlap of more than two valence orbitals for each bond. Satisfactory electron counting schemes for a given skeletal bonding topology require allocation of the available skeletal electrons and internal orbitals to the individual bonds using normally two electrons for each bond and  $n$  orbitals for a  $n$ -center bond. Difficulties can arise from uncertainties in the valence orbital manifolds and hence the electronic configurations of the vertex atoms or in the partition of vertex atom orbitals between internal orbitals participating in the skeletal bonding and external orbitals participating in bonding external to the cluster. Such difficulties can sometimes lead to ambiguities in the assignments of bonding topologies in metal clusters in case where two or more different skeletal bonding topologies assign reasonable electron configurations to the vertex atoms and use all of the available orbitals and electrons. Such ambiguities arise relatively rarely in the treatment of discrete metal clusters but occur more frequently in infinitely delocalized metal clusters such as those treated in this paper. In addition in order to provide partially filled conduction bands, highly conducting infinite metal clusters may not have enough skeletal electrons to fill all of the bonding orbitals. These ambiguities limit the applicability of graph-theory derived methods for the study of the bonding topology of infinitely delocalized metal clusters such as those discussed in this paper with the difficulties apparently increasing as the number of dimensions of infinite delocalization increases. Nevertheless, this paper is able to show that the ideas which lead to satisfactory bonding models for discrete metal clusters still lead to consistent results for infinitely delocalized metal clusters.

This paper treats metal halide clusters in which the halogen atoms are either edge-bridging ( $\mu_2$ -X) or face-bridging ( $\mu_3$ -X) and thus as neutral ligands are net donors of three and five electrons, respectively, through two and three electron pairs, respectively. In the actual three-dimensional structures the electron pairs of such halogen atoms not required for the primary bridging within a cluster octahedron or single chain of octahedra may be donated to adjacent octahedra or chains of octahedra in the actual three-dimensional structure. Such lone pairs from external halogen atoms must be considered in electron-counting schemes in order to obtain meaningful electron counts.

One of the most important points of this paper is the extension of octahedral metal cluster bonding models to infinite solid state systems. In this context the concept of a metal octahedron repeating unit is most fundamental. Atoms shared by two or more such repeating units are partitioned equally between the repeating units. Electrons and orbitals from such shared atoms may not necessarily be partitioned equally but the sums of the electrons and the orbitals donated by the atom to all of the units sharing the atom in question must equal the total numbers of valence electrons and orbitals available from the neutral atom, generally 3 or 4 electrons and 8 and 9 orbitals, respectively, in the systems discussed in this paper.

#### Discrete Octahedral Clusters

This paper considers the following skeletal bonding topologies for octahedral metal clusters:

- (1) Edge-localized: 12 two-center bonds along the 12 edges of the octahedron requiring 24 skeletal electrons and 24 internal orbitals corresponding to 4 internal orbitals for each vertex atom.

(2) Face-localized: 8 three-center bonds in the 8 faces of the octahedron requiring 16 skeletal electrons and 24 internal orbitals corresponding to 4 internal orbitals for each vertex atom. Face-localized octahedra thus require 8 skeletal electrons less than edge-localized octahedra.

(3) Globally delocalized: 6 two-center bonds delocalized in the surface of the octahedron and a single six-center bond in the core of the octahedron requiring 14 skeletal electrons and 18 internal orbitals corresponding to only 3 internal orbitals for each vertex atom. Globally delocalized octahedra are found in octahedral boranes and carboranes (e.g.,  $B_6H_6^{2-}$  and  $C_2B_4H_6$ ) as well as octahedral cluster metal carbonyls (e.g.,  $Rh_6(CO)_{16}$  and  $Ru_6(CO)_{17}C$ ).<sup>13,15</sup>

The prototypical examples of edge-localized octahedral metal clusters are the molybdenum(II) halide derivatives generically represented as  $Mo_6X_8L_6^{4+}$  including "molybdenum dichloride,"  $Mo_6(\mu_3-Cl)_8Cl_2Cl_{4/2}^{43}$ . The structures of these compounds consist of  $Mo_6$  octahedra, a face-bridging ( $\mu_3$ ) halogen atom in each of the eight octahedral faces, and one bond from each molybdenum vertex to an external ligand (L) which may be a halogen atom bridging to another  $Mo_6$  octahedron. The coordination polyhedron of each of the vertex molybdenum atoms is a 4-capped square antiprism (Figure 1) with the external ligand L in the axial position (a), four bonds to face-bridging halogen atoms in the four medial positions (m), and the four internal orbitals in the basal positions (b) forming the two-center bonds with adjacent molybdenum atoms. An L-Mo vertex using four internal orbitals and thus five external orbitals is a  $(5)(2) - 6 - 2 = 2$  electron acceptor (or -2 electron donor) after allowing six electrons from the neutral molybdenum atom and two electrons from the neutral ligand L. This leads to the following electron counting scheme<sup>15</sup>:

6 LM <sub>o</sub> vertices: (6)(-2) =	-12 electrons
8 $\mu_3-X$ bridges: (8)(5) =	40 electrons
+4 charge =	<u>-4 electrons</u>
Net skeletal electrons	24 electrons

These 24 skeletal electrons are exactly the number required for an edge-localized octahedron having 12 two-center edge bonds as discussed above.

Now consider the octahedral cluster niobium halides of the general type  $\text{Nb}_6\text{X}_{12}\text{L}_6^{2+}$  including the binary halide  $\text{Nb}_6(\mu_2\text{-Cl})_{12}\text{Cl}_{6/3}$  ( $=\text{Nb}_6\text{Cl}_{14}$ ).<sup>44</sup> The structures of these compounds consist of  $\text{Nb}_6$  octahedra, an edge-bridging ( $\mu_2$ ) halogen atom across each of the 12 octahedral edges, and one bond from each niobium vertex to an external ligand (L), which may be a halogen atom bridging to another  $\text{Nb}_6$  octahedron such as in  $\text{Nb}_6\text{Cl}_{14}$ . Again the coordination polyhedron of each of the vertex niobium atoms is a 4-capped square antiprism (Figure 1) but in this case with the external ligand L in the axial position (a), four bonds from medial positions (m) to edge-bridging halogen atoms, and four internal orbitals in the basal positions (b) to form the three-center face bonds with adjacent niobium atoms. An L-Nb vertex using four internal orbitals and thus five external orbitals is a  $(5)(2) - 5 - 2 = 3$  electron acceptor (or -3 electron donor) after allowing for five electrons from the neutral niobium atom and two electrons from the neutral ligand L. This leads to the following electron-counting scheme for  $\text{Nb}_6\text{X}_{12}\text{L}_6^{2+}$ :

6 LN <sub>b</sub> vertices: (6)(-3) =	-18 electrons
12 μ <sub>2</sub> -X bridges: (12)(3) =	36 electrons
+2 charge =	<u>-2 electrons</u>
Net skeletal electrons	16 electrons

These 16 skeletal electrons are exactly the number required for a face-localized octahedron with its 8 three-center face bonds as discussed above.

The face-bridged edge-localized  $\text{Mo}_6\text{X}_8\text{L}_6^{4+}$  clusters and the edge-bridged face-localized  $\text{Nb}_6\text{X}_{12}\text{L}_6^{2+}$  clusters may be regarded as complementary since in  $\text{Mo}_6\text{X}_8\text{L}_6^{4+}$  the halogen atoms occupy faces and the metal-metal bonds occupy

edges whereas in  $\text{Nb}_6\text{X}_{12}\text{L}_6^{2+}$  the roles of the edges and faces are reversed so that the halogen atoms occupy edges and the metal-metal-metal bonds occupy faces. These systems have also been discussed recently by Johnston and Mingos.<sup>45</sup>

There are also a number of discrete octahedral early transition metal halide clusters in which a light atom such as beryllium, boron, carbon, or nitrogen is located in the center of an octahedron of transition metal atoms such as zirconium. Thus a series of octahedral zirconium clusters is known<sup>46</sup> with the general formula  $\text{Zr}_6(\mu_2-\text{Cl})_{12}\text{ECI}_{n-12}^z$ , in which  $z = 10 - n + p_E$  with  $p_E$  being the number of valence electrons of the neutral interstitial atom E. Known isoelectronic members of this series include  $\text{Zr}_6\text{Cl}_{12}\text{Be}$ ,  $\text{Zr}_6\text{Cl}_{13}\text{Be}^-$ ,  $\text{Zr}_6\text{Cl}_{16}\text{Be}^{4-}$ ,  $\text{Zr}_6\text{Cl}_{13}\text{B}$ ,  $\text{Zr}_6\text{Cl}_{14}\text{B}^-$ ,  $\text{Zr}_6\text{Cl}_{15}\text{B}^{2-}$ ,  $\text{Zr}_6\text{Cl}_{14}\text{C}$ , and  $\text{Zr}_6\text{Cl}_{15}\text{N}$ . In these centered octahedra each zirconium vertex is bonded to five halogen atoms, four of which are edge bridging to a neighboring zirconium atom and the fifth halogen atom bridges to another  $\text{Zr}_6$  octahedron; this latter halogen may formally be regarded as a ligand (L) so that  $\text{Zr}_6\text{Cl}_{15}\text{N}$  may be treated as  $\text{Zr}_6\text{Cl}_{12}\text{NL}_6^{3+}$ . The zirconium vertices clearly use five external orbitals making them  $(5)(2) - 4 - 2 = 4$  electron acceptors (-4 electron donors). This leads to the following electron counting scheme for  $\text{Zr}_6\text{Cl}_{12}\text{NL}_6^{3+}$  and the isoelectronic derivatives mentioned above:

6 L Zr vertices: (6)(-4) =	-24 electrons
12 $\mu_2$ -X bridges: (12)(3) =	36 electrons
Interstitial N atom:	5 electrons
+3 charge	<u>-3 electrons</u>
Net skeletal electrons	14 electrons

This is the correct ( $2v + 2$  for  $v = 6$ ) skeletal electron count for a globally delocalized octahedron<sup>13,15</sup> which has one six-center core bond and six two-center

bonds delocalized over the octahedral surface. Note that this bonding topology requires only three internal orbitals from each vertex atom meaning that each vertex zirconium atom has a manifold of only eight bonding orbitals, namely five external and three (rather than four) internal orbitals. This corresponds to a 16-electron configuration similar to that found in a variety of stable zirconium compounds such as  $(C_5H_5)_2ZrCl_2$ . Also note that the presence of an interstitial atom in the center of an octahedral cluster favors a bonding topology containing a six-center core bond rather than bonding topologies having only edge and/or face bonding.

It is instructive to compare the total valence electron counts of octahedral metal clusters having the four different types of bonding topologies found in this paper and elsewhere.<sup>13,15</sup> Such electron counts consider not only skeletal (internal) electrons but also the numbers of electrons needed to fill the external orbitals. These correspond to the electron counts used in other cluster bonding models<sup>3,9-12,25-29</sup> which make no attempt to separate external and internal orbitals. In this way the following total electron counts are obtained:

A) Edge-localized Octahedron ( $Mo_6X_8L_6^{4+}$ )

Skeletal electrons:

12 two-center edge bonds: 24 electrons

External electrons:

5 external orbitals per vertex:  $(6)(5)(2) =$  60 electrons

Total valence electrons 84 electrons

B) Face-Localized Octahedron ( $\text{Nb}_6\text{X}_{12}\text{L}_6^{2+}$ )

Skeletal electrons:

8 three-center face bonds: 16 electrons

External electrons:

5 external orbitals per vertex:  $(6)(5)(2) =$  60 electrons

Total valence electrons 76 electrons

C1) Globally Delocalized Octahedron ( $\text{Rh}_6(\text{CO})_{16}$ )

Skeletal electrons:

1 six-center core bond 2 electrons

6 surface bonds 12 electrons

External electrons (18-electron vertex atoms):

6 external orbitals per vertex:  $(6)(6)(2) =$  72 electrons

Total valence electrons 86 electrons

C2) Globally Delocalized Octahedron ( $\text{Zr}_6\text{Cl}_{12}\text{NL}_6^{3+1}$ )

Skeletal electrons:

1 six-center core bond 2 electrons

6 surface bonds 12 electrons

External electrons (16-electron vertex atoms):

5 external orbitals per vertex:  $(6)(5)(2) =$  60 electrons

Total valence electrons 74 electrons

In these listings note that the face-localized octahedron (B) has two more electrons than the globally delocalized octahedron (C2). This suggests that the reported<sup>47</sup> oxidation of  $\text{Nb}_6\text{Cl}_{12}\text{L}_6^{2+}$  to  $\text{Nb}_6\text{Cl}_{12}\text{L}_6^{4+}$  can be interpreted as a change in the skeletal bonding topology from a face-localized octahedron to a globally

delocalized octahedron. In addition the cluster  $Zr_6I_{12}C^{48}$  has two more electrons than the clusters of the general formula  $Zr_6(\mu_2-Cl)_{12}ECI_{n-12}^{z+}$  ( $z = 10 - n + p_E$ ) discussed above and therefore corresponds to the electron count required for a face-localized octahedron (B) rather than a globally delocalized octahedron (C2).

#### One-Dimensional Infinite Chains of Fused Metal Octahedra

The lanthanide halides built from chains of edge-fused octahedra have the stoichiometry  $M_2Cl_3$  as exemplified by  $Gd_2Cl_3$  (Figure 2).<sup>38</sup> The metal chains in this structure have both  $Gd_6$  ( $a^2b^4$ ) octahedral cavities and  $Gd_4$  ( $a^2b^2$ ) tetrahedral cavities with twice the number of tetrahedral cavities as octahedral cavities. A repeating octahedral  $Gd_6$  unit in the chain can be represented as  $Gd_2^{a}Gd_4^{b/2}(\mu_3^{abb-Cl_4})(\mu_2^{aa-Cl_4/2})$ . The coordination polyhedron of the bridging gadolinium atoms (b in Figure 2) may be approximated by a 4-capped square antiprism (Figure 1) with an external halogen atom in the axial position, bonds to abb face-bridging halogen atoms in the four medial positions, and internal orbitals in the four basal positions. The axial gadolinium atoms (a in Figure 2) are also nine-coordinate having four internal orbitals, a bond to an external halogen atom, two bonds to halogen atoms bridging an aa edge of the tetrahedral cavity to an adjacent octahedron, and two bonds to abb face-bridging halogen atoms in the same octahedron. Both the equatorial and bridging gadolinium atoms thus have five external orbitals and are  $(2)(5) - 3 - 2 = 5$  electron acceptors (-5 electron donors) after allowing for the three electrons of the neutral gadolinium and an electron pair from the external halogen atoms (not shown for clarity in Figure 2). This leads to the following count of skeletal electrons and internal orbitals for an octahedral  $Gd_6$  unit in  $Gd_2Cl_3$



2 axial Gd: (2)(-5) =	-10 electrons	(8 orbitals)
4/2 bridging Gd: (4/2)(-5) =	-10 electrons	(8 orbitals)
4 $\mu_3$ -Cl: (4)(5) =	20 electrons	
4/2 $\mu_2$ -Cl: (4/2)(3) =	<u>6 electrons</u>	
<b>Total skeletal electrons and</b>		
internal orbitals	6 electrons	(16 orbitals)

These skeletal electrons and internal orbitals can be used in the octahedral  $\text{Gd}_6$  unit as follows:

1 six-center octahedral core bond ( $a^2b^4$ )	2 electrons	6 orbitals
2 four-center tetrahedral core bonds ( $a^2b^2$ )	<u>4 electrons</u>	<u>8 orbitals</u>
Total electrons and orbitals required	6 electrons	14 orbitals

The failure to use two of the available 16 orbitals in this bonding topology corresponds to the axial gadolinium atoms (two for each octahedral  $\text{Gd}_6$  unit) having 16-electron rather than 18-electron configurations. Also the tendency for core bonding in tetrahedral as well as octahedral cavities in even this one-dimensional infinite metal cluster contrasts with the edge-localized bonding always found in tetrahedral chambers in discrete metal clusters.<sup>1,13,15,20</sup> The closed shell electronic configuration of  $\text{Gd}_2\text{Cl}_3$  is consistent with its semiconducting energy gap  $E_g$  of approximately 1 eV.<sup>31</sup>

### Two-dimensional Infinite Sheets of Fused Metal Octahedra

Two-dimensional infinite sheets of metal octahedra occur in the graphite-like zirconium monohalides.<sup>39</sup> The structures of these systems are built from two layers of hexagonal sheets of metal atoms which form both octahedral and tetrahedral cavities. There are twice as many tetrahedral as octahedral cavities in these infinite sheet structures as in the infinite chain structure of  $\text{Gd}_2\text{Cl}_3$  discussed above. The octahedral cavities each have six internal faces and two external faces; the external faces are capped by  $\mu_3$  face-bridging halogen atoms (Figure 3). Each metal vertex is shared by three octahedral cavities. The lattice symmetry requires the coordination polyhedra of the metal vertices to have three-fold symmetry and therefore the 4,4,4-tricapped trigonal prism with  $D_{3h}$  symmetry is used. The nine valence orbitals of each vertex metal atom are partitioned into three groups of three orbitals each again reflecting the three-fold symmetry of the metal coordination. Thus for each vertex metal atom three external orbitals are used for bonds with face-bridging halogen atoms, three internal orbitals are used for core bonding in the three octahedral cavities meeting at the metal vertex in question, and three internal orbitals are used for face bonding across the external faces of the tetrahedral cavities meeting at the metal vertex in question. A zirconium vertex in such a system thus uses three external orbitals and is an acceptor of  $(2)(3) - 4 = 2$  skeletal electrons (i.e., a -2 skeletal electron donor) after allowing for the four valence electrons of a neutral zirconium atom. This leads to the following electron counting scheme for  $\text{ZrCl} (= \text{Zr}_{6/3}(\mu_3-\text{Cl})_2)$ :

6/3 Zr: $(6/3)(-2) =$	-4 electrons	(12 orbitals)
2 $\mu_3$ -Cl: $(2)(5) =$	<u>10 electrons</u>	_____
Total skeletal electrons and orbitals	6 electrons	(12 orbitals)

These 6 skeletal electrons and 12 internal orbitals can be used for the following bonding topology based on a single repeating  $Zr_6/3(\mu_3\text{-Cl})_2$  octahedral unit:

1 six-center octahedral core bond	2 electrons	6 orbitals
2 three-center face bonds across external faces of tetrahedral cavities	<u>4 electrons</u>	<u>6 orbitals</u>
Total skeletal electrons and orbitals	6 electrons	12 orbitals

The hydrogen-stabilized lanthanide monohalides<sup>37,49,50</sup> of the stoichiometry  $HLnX$  are isostructural and isoelectronic with the zirconium monohalides and therefore can have similar bonding topologies with analogous electron and orbital counting schemes.

#### Bulk Metals as Infinite Arrays of Fused Octahedra in All Three Dimensions

The analysis in the previous sections can be extended to bulk metals as infinite arrays of fused octahedra in all three dimensions. The structures can be visualized as an infinite stacking of the hexagonal metal sheets in Figure 3 into the third dimension perpendicular to the sheets. In frequently encountered metallic structures such as the cubic close packed structures these are two tetrahedral cavities for each octahedral cavity as in the infinite one-dimensional edge-fused metal octahedra chains and infinite two-dimensional edge-fused metal octahedra sheets discussed above. In a bulk metal all of the valence orbitals of each metal atom are internal orbitals. Since each metal atom is shared by six octahedral cavities and since an octahedral cavity is formed by six metal atoms, the number of valence electrons for each octahedral cavity is equal to the number of valence electrons of the metal. Formation of one multicenter bond each in each octahedral

cavity and in the two tetrahedral cavities for each octahedral cavity requires six electrons per octahedral cavity corresponding to a metal atom with six valence electrons such as chromium, molybdenum, or tungsten. This correlates with the experimental observation of maximum heat of atomization in the 5d transition series (i.e., maximum stability of the metal lattice) with the group 6 metal tungsten<sup>32</sup> as well as the role of the transition metal divide<sup>51</sup> at the group 6 metals in determining the composition, structure, and properties of certain transition metal alloys such as the beta tungsten phases. In the 3d and 4d transition series the correlations are not quite as good since the maximum heats of atomization are found with the group 5 metals vanadium and niobium rather than the corresponding group 6 metal chromium and molybdenum, respectively<sup>32</sup>; this may be related to the s-d shear hypothesis of Stone.<sup>51</sup>

### Conclusions

This paper shows how early transition metal and lanthanide halides built from octahedral metal clusters may be used as models to show how the bonding in metal clusters develops into that of the bulk metals as the octahedral fusion is made infinite in one, two, and three dimensions corresponding to chains and sheets of fused metal octahedra and finally the bulk metals themselves. Already in one-dimensional chains such as  $Gd_2Cl_3$  the electron and orbital counts are highly suggestive of multicenter core bonding within the octahedral and tetrahedral metal cavities of the chains. Although not explicitly discussed in this paper, it is also apparent that further overlap between the core bonding orbitals from the core bonds in adjacent polyhedral cavities (i.e., those sharing a face) can lead ultimately to the infinite electron delocalization responsible for many of the characteristic electrical and optical properties of metallic systems.

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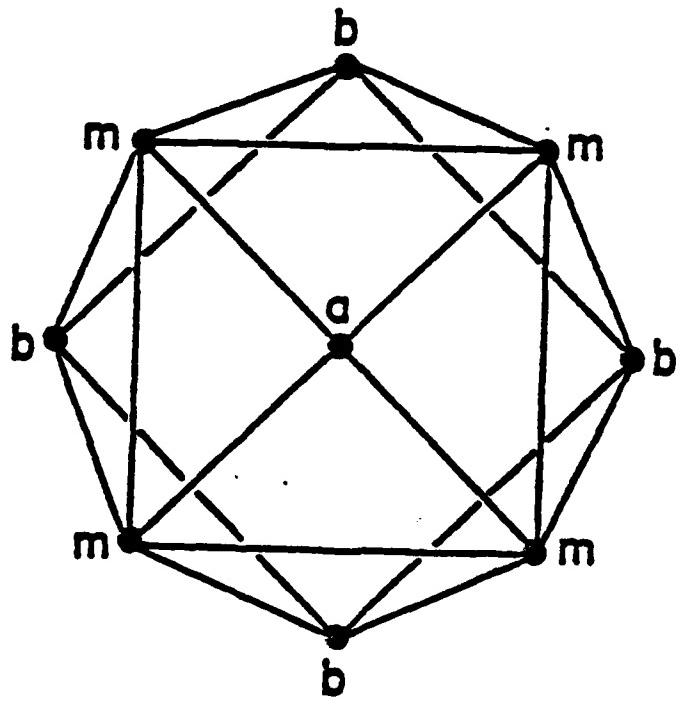
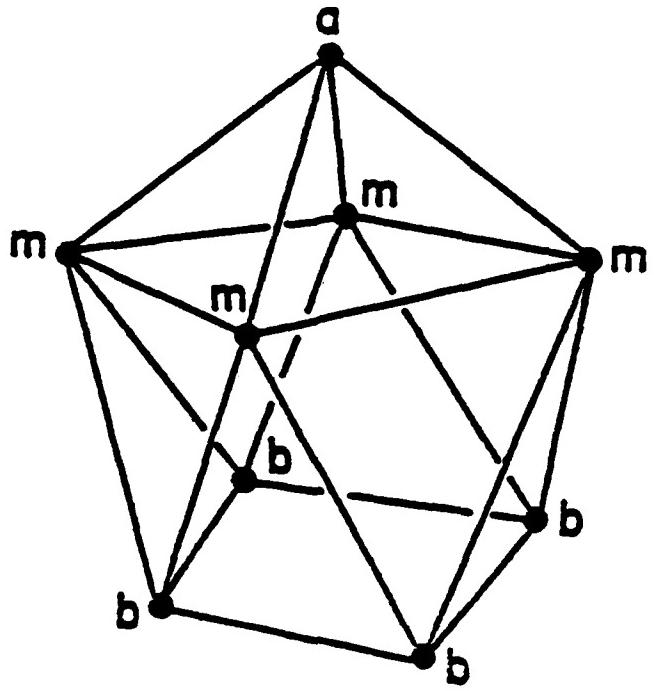
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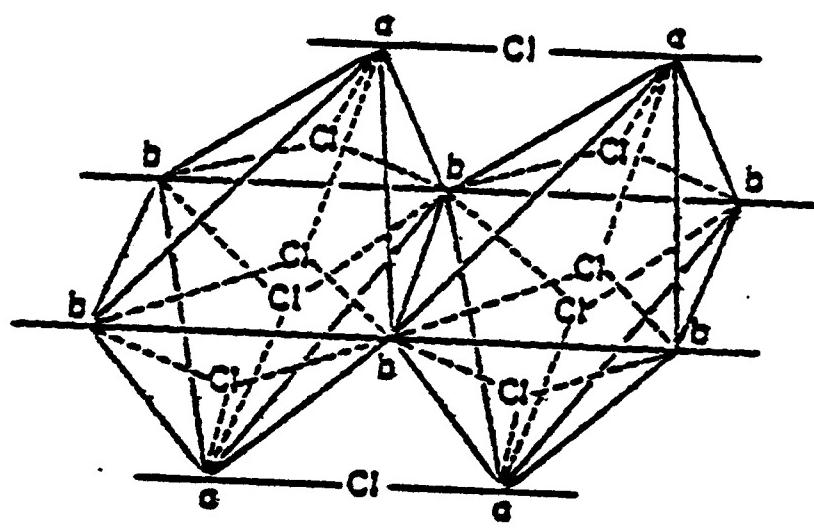
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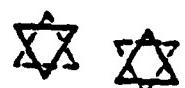
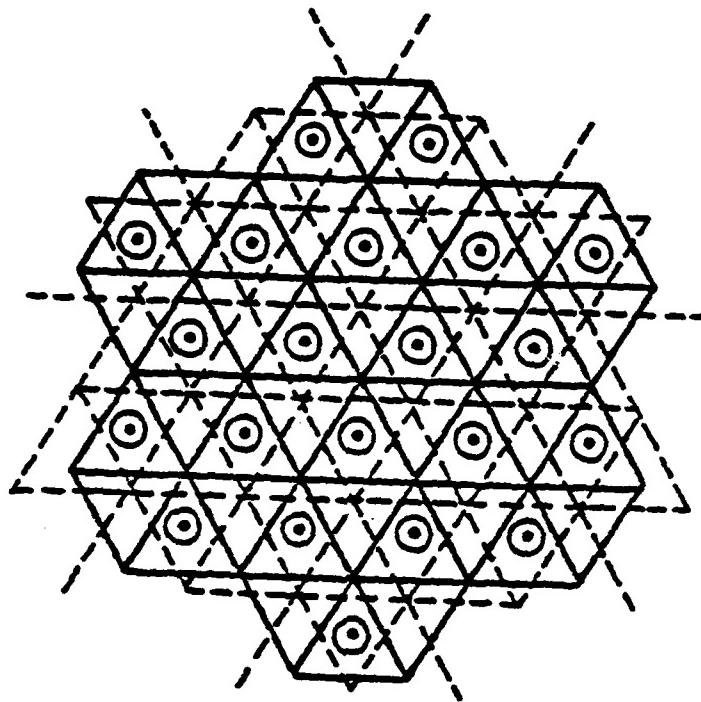
**Figure 1:** The 4-capped square antiprism showing the one axial vertex (a), the four medial vertices (m), and the four basal vertices (b). Top: side view; bottom: top view.

**Figure 2 :** Lanthanide halide structures (e.g.  $Gd_2Cl_3$ ) based on edge-fused octahedra showing a unit of two octahedra. For clarity electron pair donation from halogens in other chains to each vertex metal atom is not shown.

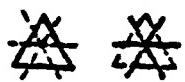
**Figure 3:** A top view of a segment of the two stacked hexagonal sheets of metal atoms in the zirconium monohalide structure. The sheet indicated in dotted lines is below the sheet indicated in solid lines. Circled dots indicate the sites of face-bridging halogen atoms above and below the sheets.







Octahedral cavities



Tetrahedral cavities



Sites of  $\mu_3$ -X atoms above and  
below the sheets

E

W

D

87

DT/C